



**WATER QUALITY MANAGEMENT**

**STANDARD OPERATING PROCEDURE**

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## **Application**

The following is the Standard Operating Procedure (SOP) of Water Quality Management (WQM) of Murray Energy Corporation (MEC). It details the SOP for proper sampling and treatment of the different forms of water encountered here by WQM (ponds, wells, streams, seeps, etc.). It also details the SOP of what to do once the proper sampling has been completed.

This SOP has been designed to facilitate the needs of Water Quality Management of Murray Energy, based on regulations established by federal and state governments.

## **Introduction**

Water sampling is an important aspect of the well being of our company. Without the results determined from our sampling, our company would not be allowed to operate to its full capacity. Our sampling provides crucial information used to show that our company is operating within the regulations put forth. This is why the proper sampling technique, supplied by this document, should be used. The results of these samples collected can only be as reliable as the sampling technique used to obtain them. The right steps should be used to secure this philosophy, and obtain results with high integrity.

Below, you will find background information and terminology found within this SOP.

### ***pH Measurements***

Out of all the analytical measurements taken throughout every branch of science and process control, pH analyses are probably the most common.

The term “pH” stands for the power of Hydrogen and is the measurement of the hydrogen ion activity in a solution. The hydrogen ion concentration is very difficult to measure directly. Instead, its activity is measured indirectly by the use of specific electrodes in the solution. These electrodes are conveniently put together to make our pH probes. The electrical potential between these two electrodes in a sample is measured, and by comparing this with the potentials of known pH samples (buffers) we can approximate the hydrogen ion activity of the solution.

As with any analytical test, you want to make sure your results are accurate and precise. You don’t want to be in violation with your NPDES permit based on inaccurate pH values. False results can be a product of improper calibration, instrument drift, improper sampling technique or a dirty probe.

At the start of every shift the pH meter should be calibrated. If pH measurements are not done that often, then calibrate before every analysis. Calibration should be done using at least three buffers. While the most common buffers for calibration are 4, 7, and 10, use ones that will cover the range of your samples. Also, buffers should be 10 times more accurate than the meter. Record all calibration data (buffers used, temperature of buffers, meter calibration settings, date/time, technician, etc.) in a field book.

Samples for pH should be grab samples and tested immediately. If samples cannot be measured directly in the field, they must be measured within 15 minutes of collection. Always rinse the end of the pH probe and blot dry before putting it into a solution.

Remember to record initials of person performing the test, date/time, location, temperature of the solution, and the pH in a field book.

In most situations, pH probes are relatively free from interference. However, all suffer from accumulated “dirt” on the glass bulb at the tip of the probe. The bulb is a glass membrane that allows certain ions in solution pass through. If the probe is responding slowly then there may be material (grease, protein, and other debris) that is blocking the flow of these ions and will need to be removed. Follow the manufacturer’s direction for cleaning the probe and how often to do so.

The pH probe should be stored wet when not in use. The type of storage solution will depend upon the recommendations of the manufacturer and the type of pH probe. However, in almost all cases a buffer or salt solution is used. Do not use distilled or deionized water as this may dilute the probe’s internal solution.

### ***Record Keeping***

#### **A. Chain of Custody**

The chain of custody procedure incorporates a number of controls to assure the integrity of a sample. These procedures, along with the required written documentation, provide you with the necessary backing to defend the integrity of the sample in any litigation. Permit violations and work-related accidents are events where proper resolution is dependent on clear and precise record keeping. Memories of events don’t count – only the records of these events and of your remedial actions do.

The chain of custody procedure starts with sample collection and follows through to the destruction of the sample. The purpose of the procedure is to ensure that the sample has been in possession of, or secured by, a responsible person at all times. It should also remove any doubt about sample identification.

This form is filled out at sample collection and follows the sample through every person involved in the chain of possession until it reaches the laboratory. It includes information such as sample number, location where sample was taken, preservative used in each container, type and size of container for each sample, dates and times of collection, type of sample, and the name of person collecting the sample, field Ph and temperature, and flow rates.

#### **B. Site Designation**

All samples must be identified with its proper site designation. This number will follow the sample through all the analyses to the final report. It should be identified on the sample on the container, the chain-of-custody form, in all data sheets, in computer entry, and reports. An example would be permit D-2291 P-001. P-001 is the designated site name for the first settlement pond in which we monitor. This is how we would identify a potential sample from this site.

#### **C. Label**

Attached to every sample will be either a label or a hand written list of the following information written in waterproof ink: taken site designation, location where sample was (OAEI, OVCC, and Century), date and time of collection, what preservation is used, permit number and your initials. It’s very important to consistently complete the labeling process each time.

#### D. Field book

Use an assigned field book with numbered pages and use permanent ink for all record keeping. Never remove a page from the book. If you make any mistakes while writing, do not erase or use “white-out,” simply draw a line through the mistake and add your initials next to it. Always keep your records neat, organized, and secure. Record in your field book all the basic information you have collected each day. The following should be listed for each site: sample designation, location, times and dates of sampling, composite sample temperature and Ph, and flow calculations. Also record anything about the sample and sampling event that you may need for future reference. These can include who you spoke to at the mine, what processes they were running at the time of sampling, weather conditions and anything else that relates to the sampling event. Field books are important especially on days when only site checks take place. For NPDES purposes, you must keep your monitoring records for at least three years.

#### TraDet Laboratories Protocol

Holding Times for Parameters Performed by TraDet Laboratories			
Parameter	Hold Time	Parameter	Hold Time
Acidity (as CaCO <sub>3</sub> )	14 Days	Mercury	28 Days
Acidity, Hot	14 Days	Molybdenum	6 Months
Alkalinity (as CaCO <sub>3</sub> )	14 Days	Nitrate (as N)	48 hours
Aluminum	6 Months	Nitrite (as N)	48 hours
Ammonia Nitrogen (as N)	28 Days	Nitrate + Nitrite	48 hours
Antimony	6 Months	Nickel	6 Months
Arsenic	6 Months	Oil & Grease	28 Days
Barium	6 Months	pH, Lab	15 minutes
Beryllium	6 Months	Phosphorus, Total	28 Days
BOD- 5 day	48 hours	Phosphorus, Ortho	28 hours
Boron	6 Months	Potassium	6 Months
Cadmium	6 Months	Selenium	6 Months
Calcium	6 Months	Silver	6 Months
CBOD - 5 day	48 hours	Sodium	6 Months
Chemical Oxygen Demand - LR	28 days	Specific Conductance	28 Days
Chemical Oxygen Demand - HR	28 Days	Strontium	6 Months
Chloride	28 Days	Sulfate (as SO <sub>4</sub> )	28 Days
Chromium	6 Months	Sulfide	7 days
Chromium, Hexavalent	24 hours	Surfactants (MBA's)	48 hours
Cobalt	6 Months	TCLP	-
Copper	6 Months	Total Coliform (MF)	24 hours
Dissolved Oxygen	15 minutes	Total Coliform (Ecoli)(Coli-ert)	24 hours
Fecal Coliform (MF)	6 hours	Total Dissolved Solids	7 days
Ferrous Iron	24 hours	Total Kjeldahl Nitrogen (as N)	7 days
Fluoride	28 Days	Total Organic Nitrogen	7 days
Hardness (as CaCO <sub>3</sub> )	6 Months	Total Residual Chlorine	15 minutes
Heterotrophic Plate Count	24 hours	Total % Solids	7 days
Iron	6 Months	Total Suspended Solids	7 days
Lead	6 Months	Turbidity	48 hours
Magnesium	6 Months	Vanadium	6 Months
Manganese	6 Months	Zinc	6 Months

Samples should be delivered between the hours of 8:30 A.M. to 4:00 P.M. Monday through Friday, unless notified ahead of time for special circumstances. Fecal and Total Coliform and Nitrate samples should be submitted on Monday through Thursday unless approved by laboratory in advance. Call the lab ahead of time if a sample requires the testing of Nitrates, due to the laboratory's need for preparation to run this test.

Any samples that require a "rush" will be charged accordingly and the laboratory should be notified ahead of delivery of such requirements.

All samples should be submitted as soon as possible after collection. This will allow ample time for laboratory work to be completed and avoid exceeding holding limits. Avoid submitting samples toward the end of the holding limits. Laboratory personnel may not be able to respond rapidly or it may require preparation for analyses which will cause the sample to exceed its holding limit.

Samples taken to the lab should be iced and at a temperature of 4 – 6°C. Samples should be verified for proper preservation by laboratory personnel. Samples need identified properly with the following on each bottle:

- Sample ID or Site ID
- Location
- Date and Time collected
- Field temperature and pH at collection
- List preservation on bottle in which is present
- Samplers Initials

Samples should contain zero headspace upon collection. Samples requiring dissolved metals analyses should be filtered in the field. We can provide filters and syringes, if required. Otherwise, laboratory filtered samples will be flagged with a qualifier.

Samples should be checked against the chain of custody to match the number of samples to the number of bottles being turned into the laboratory. We must report no flows on chain of custody therefore creating a discrepancy between the total number of sites and total number of samples.

Parameters should be clearly marked on the chain of custody indicating the specific tests required, preferably not “monthly” or “quarterly” or “special” unless approved by management.

Be sure to sign and mark the date and time in the “relinquished by” box. Also the sampler ID should be initialed.

If you need bottles prepared for sampling, please notify management ahead of time, preferably several days in advance.

Please enter through the “second door” to the left of the main entrance for bottle pick up and delivery. Management will give you a tour of the facility to show location of ice packs, bottles, calibration equipment and extra chain of custodies.

## **Methods and Procedure**

Due to the differences in the many aspects of the environment, there is not a universal sampling procedure that can be used in every scenario. The following procedure set forth by WQM, covers almost all of the scenarios applied to this company. (Note: this SOP is a general procedure, and may be altered based on specific needs or other special circumstances that may arise).

### **A. Equipment Needed for Sampling**

The following list are items needed in the proper sampling, testing, and transportation of the samples from the field to the lab:

- Field Book
- Waterproof pen
- Sample collection bottles
- Sample bottle labels
- Sample bottle preservatives
- Bailer
- Dip sampler
- Ice
- Cooler
- Tape measure
- Camera
- Chain of custody forms
- Field data sheets
- Decontamination equipment
- Maps
- Safety equipment
  - i. Gloves
  - ii. Glasses
  - iii. Proper boots
  - iv. Hard hat

### **B. Sampling Requirements**

Each site has different requirements that go along with them. Most of the time, these are site and permit specific requirements. The following are examples of some requirements that may be needed prior to sampling: site ID, sampling frequency, type of sample (proper way to fill out COC), quantity of sample (how many 125 ml, 500 ml, and 1000 ml), need of preservative, test to be performed in field, data to be recorded, and notification of anything abnormal to management.

### **C. Procedures**

Prior to sampling any body of water, pH meters should be calibrated regularly, and recorded into field book. New bottles should always be used at each site, never reuse a bottle, due to possible contamination. Bottles should also be properly labeled prior to technician sampling.

- **Pond Sampling Method**

1. When sampling from a pond, the sample should always be drawn from the ponds decant. If the pond does not have a true decant, for example uses a spill way, an area that best represents the quality of the water should be set as the sampling point. This area should avoid stagnate water, surface scum, and vegetation when possible.

2. Before filling the bottle, the bottle should first be rinsed. Once bottle is rinsed, bottle can now be filled. Be sure to avoid overfilling the bottle.

3. If preservation of the sample is required, add preservative ( $\text{HNO}_3$  – 5 drops for every 125 ml).

4. Sample should be put on ice, or taken to storage area to be placed in the refrigerator. If placed in refrigerator, the laboratory needs to be notified before 10 AM in order to arrange pick up of samples (notification only needed for samples placed at OAEI).

- **Well Sampling Method**

1. A methane check must be done prior to removing well cap, and immediately after opening, if the check is required. Methane level should be promptly reported to appropriate personnel.

2. All precautions should be taken during opening of well to prevent as much contamination as possible from entering well.

3. Purging should now be done if it is required, and allow time for the well to refill.

4. A new bailer should be used obtain sample needed. Lower bailer down cautiously.

5. Allow bailer to fill up. Slowly raise the bailer.

6. Before filling the bottle, the bottle should first be rinsed. Once bottle is rinsed, bottle can now be filled. Be sure to avoid contamination and do not overfill the bottle.

7. If preservation of the sample is required, add preservative ( $\text{HNO}_3$  – 5 drops for every 125 ml).

8. Sample should be put on ice, or taken to storage area to be placed in the refrigerator. If placed in refrigerator, the laboratory needs to be notified before 10 AM in order to arrange pick up of samples (notification only needed for samples placed at OAEI).

If well is inaccessible, sample should be obtained from a tap outside of the well. If a water softener is being used, sample should be taken prior to softening. Decontaminating the spigot nozzle should be done if a bacteria sample is needed. Once this is completed, refer to step 6 above to resume sampling protocol.



- **Springs Sampling Method**

1. Select sampling point, preferably at the cleanout. If the tank or outlet area is used, avoid areas of stagnation, surface scum, vegetation, or other contamination. If using an embankment and pipe in the outlet system, allow sediment to settle out prior to taking sample.
2. Before filling the bottle, the bottle should first be rinsed. Once bottle is rinsed, bottle can now be filled. Be sure to avoid overfilling the bottle.
3. If preservation of the sample is required, add preservative ( $\text{HNO}_3$  – 5 drops for every 125 ml).
4. Sample should be put on ice, or taken to storage area to be placed in the refrigerator. If placed in refrigerator, the laboratory needs to be notified before 10 AM in order to arrange pick up of samples (notification only needed for samples placed at OAEI).

- **Stream Sampling Method**

1. Streams should be sampled near the middle of the stream and at mid-depth. Areas of stagnation, surface scum, and vegetation should be avoided.
2. Before filling the bottle, the bottle should first be rinsed. Once bottle is rinsed, bottle can now be filled. Be sure to avoid overfilling the bottle.
3. If preservation of the sample is required, add preservative ( $\text{HNO}_3$  – 5 drops for every 125 ml).
4. Sample should be put on ice, or taken to storage area to be placed in the refrigerator. If placed in refrigerator, the laboratory needs to be notified before 10 AM in order to arrange pick up of samples (notification only needed for samples placed at OAEI).

- **Seep Sampling Method**

1. Seep should be sampled in a site that suitably shows the appropriate water quality. Avoid areas of stagnation, surface scum, and vegetation that will contaminate the sample. If an embankment and pipe is used, allow time for sediment to properly settle out before taking sample.
2. Before filling the bottle, the bottle should first be rinsed. Once bottle is rinsed, bottle can now be filled. Be sure to avoid overfilling the bottle.
3. If preservation of the sample is required, add preservative ( $\text{HNO}_3$  – 5 drops for every 125 ml).
4. Sample should be put on ice, or taken to storage area to be placed in the refrigerator. If placed in refrigerator, the laboratory needs to be notified before 10 AM in order to arrange pick up of samples (notification only needed for samples placed at OAEI).

All field measurements taken at the above locations need to be recorded in a field book. After performing the required field test, the test completed, time and date of completion, identification of technician conducting test, and the results of the test should be recorded in a field book.

After all sampling is done, the appropriate Chain of Custody should be completed. See above section “TraDet Laboratories Protocol” to review process of the Chain of Custodies.

- **Diversion Ditches and Sump Areas**

1. Record date and time of inspection.
2. Record permit number of inspection location.
3. Record pond numbers and or nearest known point (haul road).

Procedure

- Walk entire ditch, sump, or pond area.
- Inspect for the following
  - i. Large amounts of sediment in any area
  - ii. Make sure sufficient rock or rip rap is located within ditch
  - iii. Proper slope
  - iv. Any pooling or ponding within ditch
  - v. Insufficient settlement time in sumps and ponds
  - vi. Any leaks that may be present in dams, ditches or sumps
  - vii. During periods of high flow rates, note any breaches of ditches, ponds or sumps
  - viii. Note any debris such as hay bales, trees, etc. that may be restricting flow
  - ix. Check that slit fences are properly built and function as they should
  - x. If possible quantify sediment level (Settle time reduced by half)

**Note:** This Standard Operating Procedure is subject to change. This change is determined by the circumstances encountered in the field

## Emergency Information

In case of an emergency, the employee should contact his immediate supervisor as soon as possible. The employee's supervisor needs to contact the safety manager for that particular mine property. The safety manager will need to evaluate the injury to determine if it may be reportable to MSHA as well. Because of internal reporting requirements, the accident report needs completed (by supervisor) before the injured person's shift ends so it can be sent with the daily safety performance report. If it is a serious injury, time is very important because of a MSHA requirement to report it to them within 15 minutes of the injury occurrence. The mine property safety manager has an internal notification flow chart that he will use to notify senior management. The safety manager at the mine site will have to include the accident report in his daily safety performance report to Murray Energy Corporation. The following is a list of mine safety managers for each operation:

AEC - Rick Leasure (740) 391-0415

TOVCC - Rich Marcavitch (724) 255-4679

KRI - Ron Winebarger (270) 836-6980

ACC - Steve Willis (618) 841-4833

MCMI - Ron Vanhorne (740) 310-9056

OAEI – Auvil Parsons (740) 310-6951

For non mine property injuries, the employee's immediate supervisor should call Barry Milbert; (740.3913667 - human resources, at OhioAmerican Energy) since it could involve worker's compensation issues. If Barry is unable to be reached, the supervisor should contact Mike Ruble (740.310.9406). If he not available, then they should contact Paul Piccolini (740.391.6825).

If the employee is injured and is transported to the emergency room for medical evaluation and treatment, then he/she must be drug tested. There may instances as well that would require drug testing of an employee who reports an injury and does not need treatment but at the time exhibits or manifests behavior commonly known as reasonably suspicious behavior. It would then be up to the supervisor to make that determination and have testing done. Wheeling Medical Park is set up to handle Murray Energy Corporation employees who need such testing.